



# Nanocrosses of lead sulphate as the negative active material of lead acid batteries



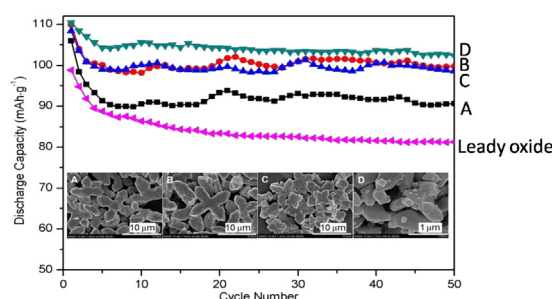
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## HIGHLIGHTS

- $\text{PbSO}_4$  can be directly used as the negative active material in lead acid batteries.
- Nanocrosses morphologies  $\text{PbSO}_4$  can be easily prepared.
- The prepared  $\text{PbSO}_4$  discharges a capacity of  $103 \text{ mA h g}^{-1}$  at  $120 \text{ mA g}^{-1}$  and remains 80% of the capacity after 550 cycles.
- Products prepared were promising electrode candidates for lead acid batteries.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Lead sulphate transforms into  $\text{PbO}_2$  and  $\text{Pb}$  in the positive and negative electrodes, respectively, when a lead acid battery is charged, thus, it is an active material. It is also generally acknowledged that sulphation results in the failure of lead acid batteries; therefore, it is very interesting to find out how to make lead sulphate more electrochemically active. Here, we demonstrate that nanocrystalline lead sulphate can be used as excellent negative active material in lead acid batteries. The lead sulphate nanocrystals, which are prepared by a facile chemical precipitation of aqueous lead acetate and sodium sulphate in a few minutes, look like crosses with diameter of each arm being  $100 \text{ nm}$  to  $3 \mu\text{m}$ . The electrode is effectively formed in much shorter time than traditional technique, yet it discharges a capacity of  $103 \text{ mA h g}^{-1}$  at the current density of  $120 \text{ mA g}^{-1}$ , which is 24% higher than that discharged by the electrode made from lead oxide under the same condition. During 100% DOD cycles, more than 80% of that capacity remains in 550 cycles. These results show that lead sulphate can be a nice negative active material in lead acid batteries.

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## 1. Introduction

Lead acid batteries occupy a half of the share in the rechargeable battery market owing to their high ratio of performance to cost [1,2]. In spite of this, there are still increasing concerns on improving of energy density [3–6], cycle life [7–9] and charge/discharge efficiency [10,11].

Currently, the materials used in lead acid battery manufacturing are lead oxide made from lead either via ball milling or by the Barton pot technique, which is typically a mixture of 20–30 wt.% metallic lead and 70–80 wt.% lead monoxide [12]. This lead oxide is heterogeneous and has grains of several micrometres big, consequently, it discharges only about  $90 \text{ mA h g}^{-1}$ , which is just about a half of the theoretical capacity of  $\text{PbSO}_4$  ( $177 \text{ mA h g}^{-1}$ ).

Conventionally, pastes for positive and negative plates are formed by mixing lead oxide powder, small quantities of additives, water and sulphuric acid. In the processes of making pastes, both the amount of free lead oxidized and basic lead sulphate formed at

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each step (e.g. paste making, pasting, and curing) are very difficult to control accurately. This leads to variations of components in the finished plates, which, in turn, affects the physical, chemical and electrochemical properties of the plates and results in problem of uniformity in terms of electrochemical properties [13]. The pastes must go through the curing and drying processes, during which the temperature and humidity have to be carefully controlled. These processes consume long time (72–84 h), require considerable space and energy, and hence increase production cost [14].

PbSO<sub>4</sub>, a well-known industrial product, has a wide range of applications [15]. It also plays a vital role in lead acid batteries, because it is formed during discharging process and consumed during charging process. However, few papers reported using PbSO<sub>4</sub> as the active material, which make it invisible to the community. Up to now, only two papers have reported about using PbSO<sub>4</sub> as positive active materials (PAM). In 2002, Yan et al. [16] prepared PbSO<sub>4</sub> from a reaction of leady powders with excessive sulphuric acid. They found that the specific energy by weight reached 37.19 and 35.47 W h kg<sup>−1</sup> at 5 h and 2 h rate, respectively, and the cycle life of 55% DOD attained 450 times in a 12 V, 10 A h battery. In 2012, Foudia et al. [17] reported that PbSO<sub>4</sub> could be served as a precursor for positive active material in the electrode. They combined the solutions of Pb(NO<sub>3</sub>)<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub> to prepare PbSO<sub>4</sub>, which discharged a highest specific capacity of 92 mA h g<sup>−1</sup> in a positive electrode. Pitifully, both papers did not tell enough detailed information. What is more, to best of our knowledge, there have been no reports on PbSO<sub>4</sub> used directly as negative active material (NAM) in lead acid battery so far.

In the last 5 years, we have developed a novel route forth recycling of spent lead acid batteries, in which all the active materials both in positive and negative electrodes are separated separately from their grids, and then converted into electrochemically active PbO. We have found the PbO is more active than the commercial leady oxide, and the process saves much energy and releases much less environmental hazards [18,19]. As we know, the materials in the negative electrodes are a mixture of PbSO<sub>4</sub> and Pb; those in the positive electrodes are PbSO<sub>4</sub> and PbO<sub>2</sub>, we are wondering if the PbSO<sub>4</sub> itself can be more electrochemically active, which could make the recycle process further simpler and save more energy and consumption. That initiates our investigation on PbSO<sub>4</sub>.

As it is generally known, both the particle size and morphology of active materials have great effect on their electrochemical properties (for example, in lead acid battery chemistry, sulphation that leads to failure of the batteries is actually the formation of big PbSO<sub>4</sub> crystals). It is important to know how they affect the electrochemical properties. PbSO<sub>4</sub> with different morphologies have been prepared through various methods, such as cube-like PbSO<sub>4</sub> precipitated in a solution of polyethyleneimine using a double jet crystallizer [20], plate-like PbSO<sub>4</sub> nanocrystal produced in micro-emulsion system [21], rod-like PbSO<sub>4</sub> obtained from a mixture of Pb(CH<sub>3</sub>COO)<sub>2</sub>·3H<sub>2</sub>O and sodium-*p*-styrene sulphonate (PSS) with constant stirring [22], highly ordered stabilized lamellar PbSO<sub>4</sub> nanocrystal with well-crystallized walls synthesized through hydrothermal treatment method [15], PbSO<sub>4</sub> crystals with almost entirely of micrometre-scale structures and branch-type can also be prepared [23].

According to the traditional technique, leady oxide needs curing to form PbSO<sub>4</sub> and 3PbO·PbSO<sub>4</sub> (3BS) or 4PbO·PbSO<sub>4</sub> (4BS). Using lead sulphate as the active material do not need that process, consequently, time, energy, human resources and machinery can be saved. Also, lead sulphate has the smallest density of all the lead compounds, which may bring out higher porosity. Table 1 lists the densities and molar volumes of some compounds, which shows that lead sulphate has the highest molar-volume. Increasing the

porosity facilitates the diffusion of the electrolyte inside the plate and thus may improve its discharge capacity.

This paper reports what we have found on PbSO<sub>4</sub> precipitated from lead acetate and sodium sulphate, and electrical performance of the as-prepared PbSO<sub>4</sub> as the negative electrode active material.

## 2. Experimental

### 2.1. Material preparation

The nanocrystalline PbSO<sub>4</sub> was obtained as follows: 0.01 mol of Pb(CH<sub>3</sub>COO)<sub>2</sub>·3H<sub>2</sub>O together with 0.3 wt.% different surfactant: (A) none; (B) poly(sodium-*p*-styrenesulphonate) (PSS); (C) sodium dodecyl sulphonate (SDS); (D) poly(vinyl pyrrolidone) (PVP) were dissolved in 200 mL of distilled water at 70 °C, then poured into 100 mL of 0.1 mol L<sup>−1</sup> Na<sub>2</sub>SO<sub>4</sub> solution with stirring. The mixture was kept at 70 °C for another 10 min, and then the solid was filtered out, washed several times with distilled water, and dried overnight at 70 °C.

### 2.2. Characterization

Powder X-ray diffraction (XRD) patterns of the samples were conducted using a Bruker D8 Discover instrument operating at 40 kV and 20 mA, by using CuKα radiation (λ = 0.15406 nm). Scanning electron micrographs (SEM) of samples were carried out on a Hitachi S-4800 microscope.

### 2.3. Electrode preparation

The conventional leady oxide paste was prepared by mixing 1.0 g leady oxide (obtained from Huaifu Holding Group), 0.003 g of graphite, 0.02 g of BaSO<sub>4</sub>, 0.12 mL of distilled water and 0.12 mL of sulphuric acid (36 wt.%) were added to it slowly. The procedure included placing the required amount of leady oxide and additives in a container, and grinding for about 5 min to make a good dispersion. Then, sulphuric acid was added slowly with grinding; finally, the water was added to the mixture, and grinded for another 5 min.

Pastes based on the PbSO<sub>4</sub> were prepared by mixing 1.0 g of an as-prepared sample (A, B, C, or D) and 0.03 g of conducted graphite and acetylene black, respectively, 0.02 g of BaSO<sub>4</sub>, 0.006 g of lignosulfonate together with 0.14 mL of distilled water. The other procedures were the same as the conventional ways. Because lead sulphate has low electrical conductivity, more conductive additives were added to make pastes.

The plates were obtained by applying the paste evenly onto a Pb–Ca alloy grid with dimensions of 10 × 8 × 2 mm<sup>3</sup>. After pasting, the conventional leady oxide-based plate was put into an oven maintained at 50 °C with relative humidity >95%. The curing was conducted for 36 h. After that, the plate was dried at 70 °C for 48 h; while the PbSO<sub>4</sub> based plates were only need 24 h for drying at 70 °C. The mass of the active material for the calculation of the densities was the mass of the dried plate minus that of the blank grid.

**Table 1**  
Densities and molar volumes of some lead compounds.

| Lead compounds                           | Density (g cm <sup>−1</sup> ) | Molar volume (cm <sup>3</sup> mol <sup>−1</sup> ) |
|------------------------------------------|-------------------------------|---------------------------------------------------|
| PbSO <sub>4</sub>                        | 6.32                          | 48.2                                              |
| PbO·PbSO <sub>4</sub>                    | 7.02                          | 38.0                                              |
| 3PbO·PbSO <sub>4</sub> ·H <sub>2</sub> O | 6.50                          | 38.0                                              |
| Pb                                       | 11.34                         | 18.27                                             |

## 2.4. Electrochemical performance test

One negative plate was directly assembled between two commercial positive plates with separators (absorptive glass-mat, AGM) in between. They were inserted into a commercial battery case, and two separate polycarbonate fixing plates were added to provide the required plate-group pressure. An amount of  $\text{H}_2\text{SO}_4$  solution (1.23 relative density) was added and the total cell volume was held constant (plates, separator and electrolyte). The cell was then sealed. The batteries were dipped in a water bath with the temperature maintaining at  $32 \pm 2^\circ\text{C}$ .

After immersing the plates in the electrolyte for 2 h, the battery formation was carried out by three steps. Firstly, the electrode was charged at a constant current density of  $30\text{ mA g}^{-1}$  for 140 min; followed by charged at  $45\text{ mA g}^{-1}$  for 120 min; and finally, it was charged at  $60\text{ mA g}^{-1}$  for 140 min. The formation took about 400 min, followed by a 5 min rest, then for a total of 50 cycles. Since the capacity of the positive plate was substantially greater than that of the negative plate, the cell was negative electrode limited. The total input capacity was always  $120\text{ mA g}^{-1}$  versus the negative active material.

All the formation and the cycling tests were carried out with an NEWARE Cycler (BTS-5V3A Shenzhen NEWARE Electronics Co., Ltd., China). The cell was discharged at a current density of  $120\text{ mA g}^{-1}$  until the terminal voltage fell to 1.75 V. Then, it was used for cyclic tests. Both charge current and discharge current were  $120\text{ mA g}^{-1}$ , and one whole cycle took about 140 min.

The cyclic voltammetry (CV) tests were carried out on the CorrTest model CS350 electrochemical working station (WUHAN CORRTEST Instrument Co., Ltd., China). The CV curves were determined with a classical three-electrode system. A double platinum foil electrode was used as the counter electrode, and the  $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$  (sat.) was employed as the reference electrode. The measurement was carried out from  $-1.8\text{ V}$  to  $0\text{ V}$  at a potential scan rate of  $50\text{ mV s}^{-1}$ . All experiments were carried out at room temperature in  $1.23\text{ g mL}^{-1}\text{ H}_2\text{SO}_4$  solution.

## 3. Results and discussions

### 3.1. Characterization of the samples

XRD patterns of the samples prepared through different approaches are presented in Fig. 1. All diffraction peaks can be indexed with a primitive orthorhombic cell, and the parameters are  $a = 6.96\text{ \AA}$ ,  $b = 8.47\text{ \AA}$  and  $c = 5.40\text{ \AA}$ , which is the same as standard data (JCPDS No. 36-1461). Consequently, phase pure  $\text{PbSO}_4$  was obtained. It is interesting to see that the peak at  $2\theta = 33^\circ$  of the XRD patterns of samples A and B are much stronger than the others', which may indicate samples A and B have severer preferred orientation. The crystallite sizes of  $\text{PbSO}_4$  have been calculated by using Sherrer method (FWHM). The results are shown in Table 2, which also includes the apparent densities of the prepared lead sulphate samples. It can be seen that samples A–D are smaller and smaller, so are the apparent densities.

The morphologies of as-prepared  $\text{PbSO}_4$  are shown in Fig. 2. It can be seen that samples A, B and C are mostly crosses, although some of them are broken into smaller pieces. Sample D is much irregular and smaller. As sample A was prepared directly from lead acetate and sodium sulphate without using crystallization modifier, we can conclude that PSS has little effect on crystallization of sample B. Both of them are symmetrical crosses with a diagonal length of  $10\text{ }\mu\text{m}$  and arm diameter of  $2\text{ }\mu\text{m}$ . SDS can make the cross (sample C) a bit smaller and fatter (diagonal length less than  $8\text{ }\mu\text{m}$ , diameter  $2\text{--}3\text{ }\mu\text{m}$ ), but PVP totally destroys the crosses and makes it much smaller (sample D). The sample D is rod-like and plate-like,

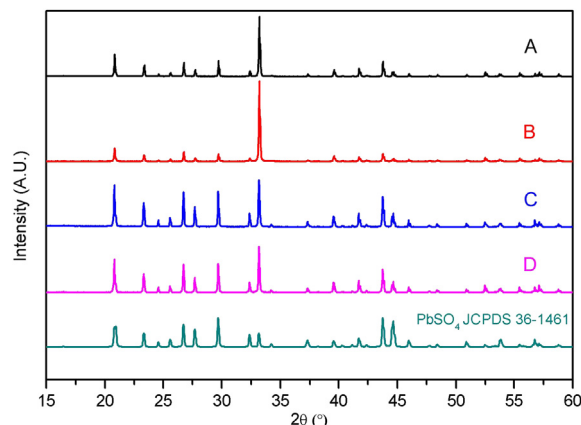


Fig. 1. XRD patterns of samples prepared with different crystallization modifiers: (A) none; (B) PSS; (C) SDS; (D) PVP.

and the biggest dimension is less than  $1\text{ }\mu\text{m}$ . It seems that the morphologies of the first three samples may be related to  $-\text{SO}_3^-$  group as the modifier. But it still needs more work to find out the reason.

### 3.2. Electrochemical performance

The plots of discharge capacity versus the cycle number for the samples are shown in Fig. 3. The electrode based on factory leady oxide is also shown for comparison. The measurements were all carried out under a current density of  $120\text{ mA g}^{-1}$ . The capacity value is determined for the NAM, and the capacity of positive electrode used was much bigger than the negative electrode. All electrodes discharge higher capacities initially, which are falling lower and soon getting stable. The leady oxide from the manufacturer gives a capacity of  $98\text{ mA h g}^{-1}$  at first, and then it becomes lower and stabilizes at about  $80\text{ mA h g}^{-1}$  in 20 cycles. However, the discharge capacities of four samples prepared here are higher than  $105\text{ mA h g}^{-1}$  firstly, and then stabilize at more than  $90\text{ mA h g}^{-1}$ . The highest capacity, which is obtained from sample D, is  $110\text{ mA h g}^{-1}$  at the first cycle and stabilizes at around  $103\text{ mA h g}^{-1}$  after only five cycles. Therefore, the electrochemical property of as-prepared  $\text{PbSO}_4$  is better than the traditional leady oxide.

According to the SEM images, the particles of sample D are less than  $1\text{ }\mu\text{m}$  mostly, but all the other samples are bigger than  $2\text{ }\mu\text{m}$ . We know that  $\text{PbSO}_4$  is an insulator. The big size of particles is not good for electron conduction, and it is vital for utilizing them. Consequently, we believe that the size of the particles has great influence on its properties here. It is also interesting to observe the behaviour of sample A and sample B, as they are about the same size and shape, but sample B still has a better activity. More research is needed to find out the reason. Under our measuring system, about 10 cycles can be made each day. The fluctuations of capacity are probably because of the temperature variation.

Table 2  
The apparent densities and the crystallite sizes of  $\text{PbSO}_4$  samples.

| Sample | Apparent density ( $\text{g cm}^{-3}$ ) | Crystallite size (nm) |
|--------|-----------------------------------------|-----------------------|
| A      | 2.31                                    | 88                    |
| B      | 1.42                                    | 72                    |
| C      | 1.49                                    | 76                    |
| D      | 1.26                                    | 58                    |



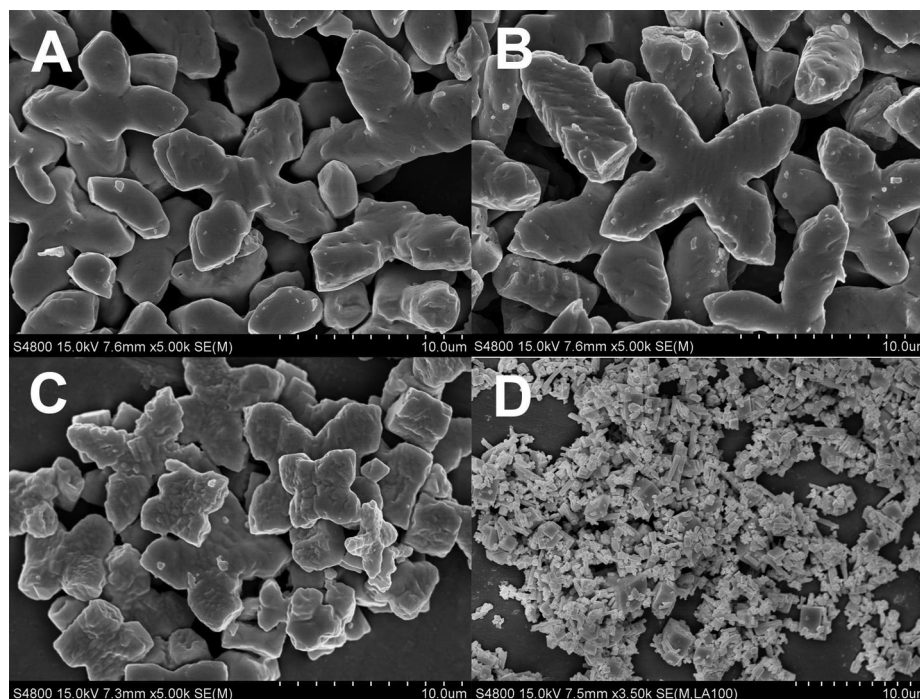


Fig. 2. SEM images of the  $\text{PbSO}_4$  samples prepared with different crystallization modifiers: (A) none; (B) PSS; (C) SDS; (D) PVP.

Fig. 4 gives the relationship between the capacity of NAM and crystallite size of  $\text{PbSO}_4$ , which shows that the smaller the crystallite size is, the bigger the capacity of NAM is. This is normal to all the electrode active materials [5].

Fig. 5 shows the discharge curves of potential versus capacity at a current density of  $120 \text{ mA g}^{-1}$  during the 20th cycle. The 20th discharge capacities of the four samples are in the range of  $92\text{--}104 \text{ mA h g}^{-1}$ . If the utilization of active material is defined as the ratio of the discharge capacity to theoretical capacity of  $\text{PbSO}_4$ , which is  $177 \text{ mA h g}^{-1}$ , those of the four samples are about 52%, 55%, 56% and 59%, respectively. In consideration of the big current density employed here, the utilization is quite acceptable, although there are still more works to do to improve it. Sample D has the smallest crystal size and presents the best electrochemical performance. So take an overall consideration, we choose sample D to do the following research.

### 3.3. Further characterization

After immersing in the electrolyte for 2 h, the plate made from sample D was charged thoroughly to activate the material. Fig. 6 gives the XRD pattern of the active materials in the plate after formation. We can see that most of the  $\text{PbSO}_4$  has transformed into Pb, some changed into 3BS, and only a little part is remained. Table 3 shows the approximate phase composition of the NAM.

Fig. 7 shows the SEM image of the electrode material after formation. There are some rod-like nanoparticles as well as big lamellar and irregular particles. Those lamellar and irregular particles should be carbon; the rod-like nanoparticles are metallic lead [24].

Fig. 8a shows the influence of current density on the discharge capacity. It can be seen that the discharge capacity varies a little when the discharge current density is ascertained, although the

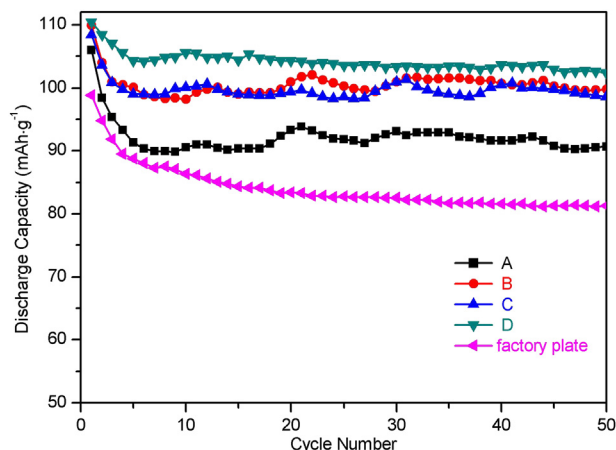


Fig. 3. The discharge capacity curves of the lead sulphate plate and leady oxide plate at the current density of  $120 \text{ mA g}^{-1}$ .

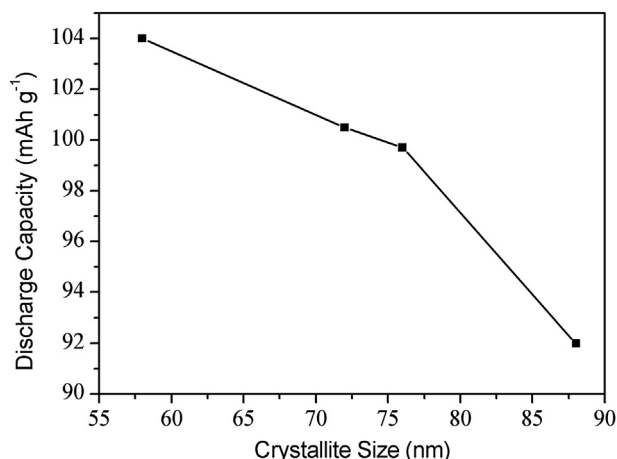


Fig. 4. The effect of  $\text{PbSO}_4$  crystallite size on the capacity of NAM.

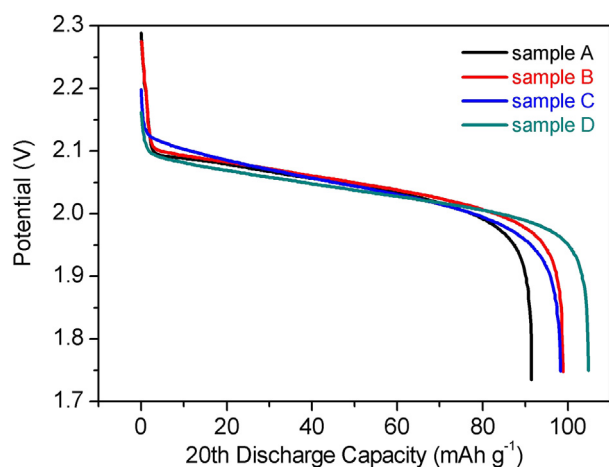


Fig. 5. The 20th discharge curves of potential versus capacity.

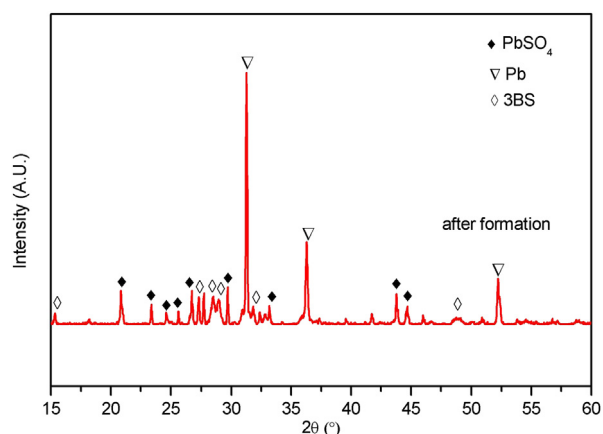


Fig. 6. XRD pattern of the paste based on sample D after formation.

**Table 3**  
The composition of sample D after formation.

| Composition (wt.%) |                   |      |
|--------------------|-------------------|------|
| Pb                 | PbSO <sub>4</sub> | 3BS  |
| 95.41              | 2.44              | 2.14 |

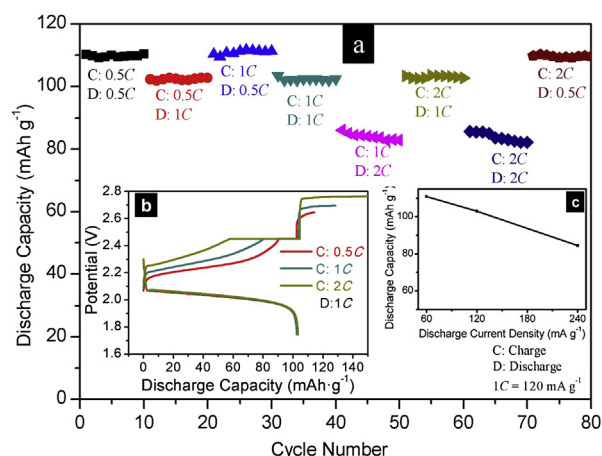


Fig. 8. (a) The discharge capacity of lead sulphate electrode at different constant current densities; (b) the curves of potential versus discharge capacity of the PbSO<sub>4</sub> sample at different charge current densities under the same discharge current density; (c) the curve of the battery discharge capacity versus discharge current density.

current density for charge increased from 0.5 C to 2 C ( $1\text{ C} = 120\text{ mA g}^{-1}$  here). Fig. 8b gives curves of potential versus discharge capacity of the PbSO<sub>4</sub> sample at different charge current densities under the same discharge current density of  $120\text{ mA g}^{-1}$ . It is obvious that the discharge curves are almost the same regardless of the different charging procedures. From Fig. 8c, we can learn that the discharge capacity presents a nearly linear decrease as the current density changes. Considering the much longer time consumed at low current density, we chose 1 C as the current density for both charge and discharge procedures.

Under the system of charging and discharging, the cyclic stability of the electrode was tested for over 550 cycles. From Fig. 9, we can see that the electrode discharges less and less capacity in cycles of 100% DOD, and 80% of the first discharge capacity comes at the 450th cycle. However, if that is recalculated according to the stabilized capacity ( $103\text{ mA h g}^{-1}$ ), 80% of the capacity emerges at the 550th cycle. It is very remarkable in lead acid batteries [24–26].

Voltammetry tests were conducted in the potential range from 0 V to  $-1.8\text{ V}$  (vs. Hg/Hg<sub>2</sub>SO<sub>4</sub> electrode in saturated K<sub>2</sub>SO<sub>4</sub>) at a scan rate of  $50\text{ mV s}^{-1}$ . The obtained voltammograms are presented in Fig. 10. The figure presents the CV curves of both the lead sulphate electrode and lead oxide electrode at 50th cycle. It can be seen that the reduction of PbSO<sub>4</sub> to Pb occurs at  $-1.5\text{ V}$ , the evolution of hydrogen occurs below  $-1.65\text{ V}$ , and the oxidation of Pb to PbSO<sub>4</sub> is at  $-0.68\text{ V}$ . The oxidation peak is much stronger

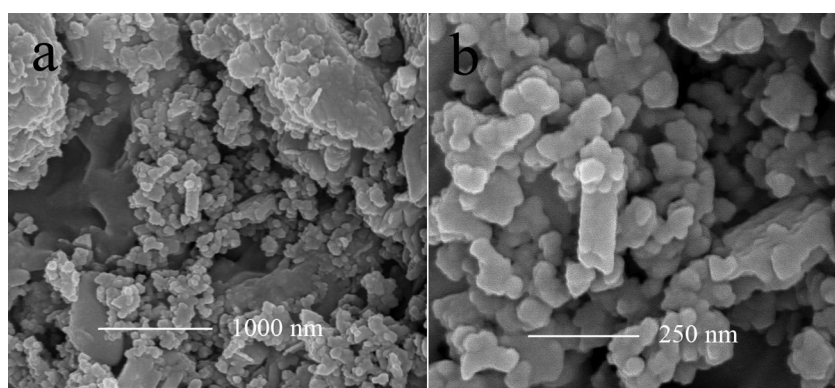


Fig. 7. SEM images of the paste based on sample D after formation at different magnifications.

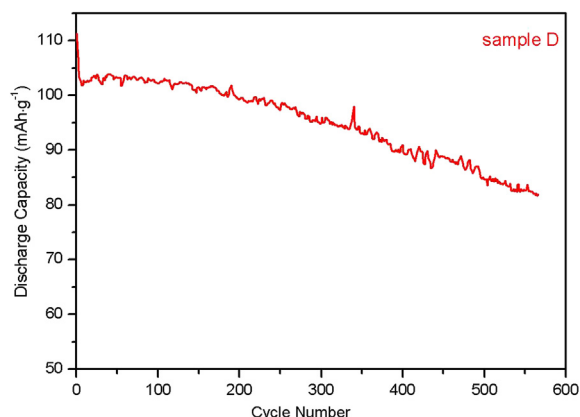


Fig. 9. The cycle life test of the lead sulphate based battery.

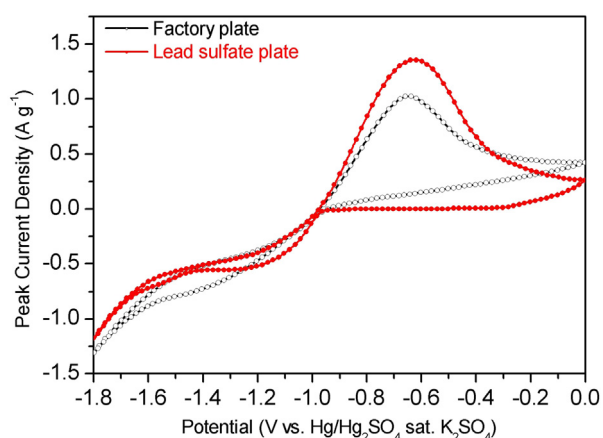


Fig. 10. Cyclic voltammetry curves of the lead sulphate plate and lead oxide plate.

than the reduction peak. This is because of the difference in conductivities of Pb from  $\text{PbSO}_4$ . Pavlov [27] suggested that the decreasing peak current originated from the diminishing surface area due to the formation of a less porous film during the cyclic process. Therefore, it can be deduced in the present study that the electrode based on lead sulphate can inhibit the growth of the anodic  $\text{PbO}$  film at Pb electrode and slow down the corrosion of Pb substrate, which ensures a better conductivity of the anodic film on grid in lead acid batteries [8].

#### 4. Conclusion

The lead sulphate with crystal size of 100 nm to 3  $\mu\text{m}$  in the smallest dimension can be easily prepared by a chemical precipitation of  $\text{Pb}(\text{CH}_3\text{COO})_2$  with  $\text{Na}_2\text{SO}_4$  in 10 min at 70 °C. When sulphate or sulphonate exists, the micro-crosses  $\text{PbSO}_4$  is formed, but when PVP is used as the crystallization modifier, it is irregular and in smaller size.

When  $\text{PbSO}_4$  is used as the negative active material, preparation of the electrode takes only 1/3 of the time as used for the traditional lead oxide. This definitely saves electrical energy, human resources and machinery.

The electrochemical performance of the  $\text{PbSO}_4$  is also better than that of the lead oxide. While the traditional lead oxide electrode gives a stable capacity of about 80  $\text{mA h g}^{-1}$ , the as-prepared  $\text{PbSO}_4$  may present a stable discharge capacity as high as 103  $\text{mA h g}^{-1}$ . During 100% DOD cycles of charge and discharge at 120  $\text{mA g}^{-1}$ , 80% of that capacity comes after 550 cycles. These results show that lead sulphate can be a nice negative active material for lead acid batteries.

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